SOME PHYSICO-CHEMICAL STUDIES ON GALLIUM AND THALLIUM COMPOUNDS

BY

GLENDALL LEE KING

B.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

The elements gallium, indium, and thallium are more plentiful than is generally realized. However, their development and use have always been restricted because of the paucity of knowledge about them. Any contribution to basic knowledge relating to them may aid in future development.

Among the characteristics of the gallium-indium-thallium family essential to their systematic study are trends and variations in basicity. The combined effects of small size and comparatively high charge among the tripositive ions of these elements should render them somewhat acidic in character, but significant differences should be discernable among these ions as these factors vary.

In evaluating such trends, the technique of electrometric titration with standard alkali and measurement of hydrogen ion concentration as a function of salt concentration have been employed. Previously reported measurements of these types have been limited in number and lacking in agreement. For example, addition of sodium hydroxide to gallium(III) chloride solutions have been said to start precipitation of the hydrous oxide at pH values ranging from 2.8 to 3.5, while the ratio of hydroxyl ion to gallium ion necessary for the beginning of this precipitation varied from about 1.0 to 2.6(3,4). Hydrolysis studies on gallium(III) salt solutions appear to be limited to those of Fricke and his coworkers (2,3), while competent quantitative studies on thallium(III) salt solutions do not appear to have been reported. In addition, the high temperature reactions of gallium(III) oxide with other more basic oxides were investigated.

Data already are existent along this general line for indium (III) compounds (5,6,7), and it was the purpose of this

investigation to obtain corresponding data for gallium(III) and thallium(III) compounds, with the hope that the information obtained would be useful in elucidating the general chemistry of this family.

Experimental And Discussion

Electrometric titration data were obtained by the standard procedure (6), using a Beckman Model H pH Meter, the glass electrode of which was checked frequently against a 0.05 M potassium acid phthlate buffer. Hydrolysis measurements were made by determining pH values as functions of concentration (5,7). For all measurements, solutions were maintained within $\pm$ 0.2° of the stated temperature by thermostating.

Data were obtained for electrometric titrations with sodium hydroxide of gallium(III) sulfate solutions varying from 0.099 to 0.229 M in gallium ion at temperatures of 10°, 25°, and 40° C. It was shown that, regardless of temperature, roughly one mole of hydroxyl ion to each mole of gallium ion was necessary for precipitation incidence. The average values for these ratios are at 10°, 1.08; at 25°, 0.99; and at 40°, 0.83. Precipitation pH values are essentially independent of concentration at a given concentration but decrease with temperature increase, average values of 3.02, 2.77, and 2.63 being found at 10°, 25°, and 40° C., respectively.

Data characterizing complete dissolution of the precipitates are subject to somewhat greater variations. In general, between five and six moles of hydroxyl ion were required per mole of gallium to cause dissolution. These mole ratios are probably without real significance, for dissolution, like precipitation, was undoubtedly spread over a considerable interval. It seems reasonable to expect considerable hydrolysis in gallate solutions, and the total quantity of hydroxyl ion required to effect complete dissolution is doubtless the sum of the quantity necessary for gallate formation and the quantity necessary to prevent precipitation by hydrolysis.

For convenience in evaluation of the solubility product constant and water solubility the precipitated material was considered to be the hydroxide. Application of the conventional treatment (1), without use of activities, at various hydroxyl to gallium ion ratios in the precipitation regions of the titrations yielded solubility product constants of the order of 10^{-35} with corresponding water solubilities of the order of 10^{-10} gram mole per liter.

Corresponding data were obtained at 25° C. for 0.020 to 0.150 M gallium(III) bromide solutions, for 0.010 to 0.150 M gallium(III) chloride solutions, and for 0.010 to 0.123 M gallium(III) nitrate solutions. While the curves obtained for the bromide, chloride, and nitrate are similar to those obtained with sulfate solutions, precipitation incidence is markedly different. With bromide, chloride, and nitrate, nearly 3.0 moles of hydroxyl ion were required per mole of gallium ion before visible precipitation occurred, yet the plateaus in the titration curves indicate steady consumption of hydroxyl ion up to these points. Polarographic investigations of such solutions indicated that as base is added, hydroxy-gallium ions of increasing complexity are built up until the mole ratio of the hydroxyl to gallium ion approaches 3.0, at which time the gallium precipitates out.

Because of the uncertainties characterizing precipitation from bromide, chloride, and nitrate solutions, evaluation of solubility product constants were not attempted. Data on dissolution of the precipitates in excess hydroxyl ion are in excellent agreement with those found for the sulfate solutions.

Electrometric titrations were carried out on sulfuric acid solutions of thallium(III) sulfate, varying in thallium ion concentration from 0.0581 to 0.219 M, at 10°, 25°, and 40° C. Although valid hydroxyl to thallium ion ratios could not be assigned, thallium(III) oxide was found to precipitate at definite pH ranges with the average pH of precipitation being 1.01 at 10°, 0.99 at 25°, and 1.14 at 40°. Solubility product constants calculated on the basis of modified hydroxyl to

thallium ion ratios were of the order of 10^{-37} with a corresponding water solubility of 10^{-10} gram mole per liter.

Similar data were obtained at 25° C. for 0.010 to 0.150 M thallium(III) bromide and chloride solutions. However, precipitation incidence of hydrous thallium(III) oxide took place at considerably higher pH values with average values of 3.63 and 3.29 being found from bromide and chloride solutions respectively. Calculated solubility product constants of the order of 10^{-27} and 10^{-33} and water solubilities of the order of 10^{-7} and 10^{-8} also varied quite widely from those obtained from sulfate solutions. This wide variance can probably be best explained by the fact that trivalent thallium tends to exist in bromide and chloride solutions in the form of anionic complexes, while this tendency apparently isn't as pronounced in sulfate solutions.

Hydrolysis studies were limited to gallium(III) bromide, chloride, and nitrate solutions and to thallium(III) bromide and chloride solutions. Bromide, chloride, and nitrate were selected as being sufficiently weakly basic in character as to contribute comparatively nothing to any observed alterations in the hydrogen ion concentration in the solutions. Under these conditions any alterations could be ascribed to the acidic characteristics of the metal ion. Decision as to the mechanism governing the hydrolytic process is best based upon the constancy of the hydrolysis constant as calculated from experimental data. It appears that the hydrolysis of gallium-(III) and thallium(III) ions, like the indium(III) ion (5,7), can be expressed best by the reaction $M^{+++} + H_2O \leftrightharpoons MOH^{++} + H^+$. Hydrolysis constants of 4.6×10^{-4}, 4.1×10^{-4}, and 3.7×10^{-4} were calculated for gallium(III) bromide, chloride, and nitrate solutions, respectively, and of 4.2×10^{-3} and 3.3×10^{-3} for thallium(III) bromide and chloride solutions, respectively.

Some high temperature reactions of gallium(III) oxide and other more basic oxides were also carried out. In general, the materials formed spinel-type compounds of the general

formula MGa_2O_4, obtained by sintering mole-to-mole mixtures of the gallium(III) oxide with either the oxide of another metal or a compound of that metal which decomposes to the oxide at high temperatures. Compounds where M stands for Ba, Cu, Cd, Mg, Sr, and Zn were prepared. In addition, the compound $LaGaO_3$ was prepared.

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VITA

The author was born in Eldorado, Illinois, on April 2, 1927. He received his elementary and high school education in the public schools of that city, graduating from the Eldorado Township High School in May 1944. As a member of the Navy V-12 program he attended Illinois State Normal University from July 1944 to June 1945 and the University of Illinois from July 1945 to June 1946. After his discharge he returned to the University of Illinois and was awarded the degree of Bachelor of Science in June 1947. Immediately thereafter he entered the Graduate School of the University of Illinois. From June 1947 to September 1949, he held the position of Research Assistant on the University of Illinois Gallium Research Program sponsored by the Office of Naval Research of the United States Navy.

The author is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, Pi Mu Epsilon, and Alpha Chi Sigma.